Contract n68171-00-m-6199

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Mrs. Carole O'Connor

Dear Mrs. O'Connor:

I am faxing to your office my report 'DEVELOPMENT OF A PROGRAM TO CALCULATE LIQUID-LIQUID PHASE EQUILIBRIA IN MULTICOMPONENT SYSTEMS CONSIST OF ORGANIC SUBSTANCES', developed under the project R&D 8968-EN-01.

Please, confirm a receiving the report.

Sincerely yours

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30 April, 2001.

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1+6 pages

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report on the project R&D 8968-EN-01

'DEVELOPMENT OF A PROGRAM TO CALCULATE LIQUID-LIQUID PHASE EQUILIBRIA IN MULTICOMPONENT SYSTEMS CONSIST OF ORGANIC SUBSTANCES'.

Abstract: This report documents a Fortran version of a chemical thermodynamic model for calculating liquid-liquid equilibria in mixtures of organic compounds. The model applies the Gibbs energy minimization method for phase equilibria computation combined with the UNIFAC routine and thermodynamic database for calculating activity coefficients of organic substances in multicomponent organic liquids on the basis of the group contribution theory. The model can be extended without modifications of the Gibbs energy minimization program to take into account also chemical interactions between organic components.

1. Statements of the task.

A task to calculate a phase composition of multicomponent organic liquid mixtures is a part of more general task to calculate chemical equilibrium composition of multicomponent system. Because of this, in spite of the components at specified conditions are considered as inert ones (in other words they do not interact each with other), to keep generality we will use the terms of chemical equilibrium.

We have a system consists of N organic compounds (components) at specified temperature and pressure. The total amount of every ith compound is equal to B_i. It takes to determine a number P of the phases in the system, concentrations x_{ij} of any ith component in every jth phase, and masses of the phases X_j ($j=1,P$) in the system. It is assumed that any component is present in every coexisting phase.

2. Thermodynamic conditions of multicomponent equilibria.

The necessary and sufficient condition of multicomponent heterogeneous equilibrium is that the Gibbs energy of the system G is minimum under the balance constrains. The Gibbs energy function of the system is as follow:

$$\frac{G}{RT} = g = \sum_{j}^{P}\sum_{i}^{N} n_{ij}(\mu_{ij}^{\circ} + \ln(a_j)) \tag{1}$$

where a_{ij} is activity, n_{ij} is the amount, and μ_{ij}° is the standard chemical potential of ith component in jth phase. If we consider the components as inert ones and that the components have the same standard potential in any phase, the values of zero can be assigned to these parameters.

Activity of the components can be expressed as $a_{ij} = x_{ij}\gamma_{ij}$, where $x_{ij} = \dfrac{n_{ij}}{X_j} = \dfrac{n_{ij}}{\sum\limits_{i=1}^{N} n_{ij}}$ is

a mole fraction of the component i in the phase j, γ_{ij} is activity coefficient.

The consequence of the condition of a thermodynamic equilibrium is that the chemical potential for each ith component must be the same in any jth phase. If every component has the same standard potential μ° in any phase it leads to equality of activities:

$$x_{i1}\gamma_{i1} = x_{i2}\gamma_{i2} = ... = x_{iP}\gamma_{iP} \qquad (2)$$

Mass balance constrains may be written as a system of liner equations:

$$\sum_{j=1}^{P} n_{ij} \cdot v_{ij} = B_i, i = 1, N \qquad (3)$$

where v_{ij} is a stoichiometric coefficient, that shows a number of independent components j in the component i. If we choose as independent components real components of the system then $v_{ij} = \ .$

It can be shown by liner transformations that $P \leq N$ (The Gibbs phase rule)

<u>Summary of the algorithm of the Gibbs energy minimization.</u>

The applied algorithm of search of the global minimum of the function (1) under constrains (3) combines methods of linear and nonlinear programming. It is very close to the algorithm applied by de Capitani and Brown, 1987

<u>The initial phase assemblage.</u>

We start with a feasible assemblage of N linearly independent pure phases consisted of only one component each. The amount of each ith phase is equal to B_i. Thus the mass balance equations are satisfied.

<u>Step 1. The nonlinear programming</u>

At the first step we suppose that every jth potential phase has the following composition: $x_{ij}=0.95$ if $i=j$ and $x_{ij}=(1-0.95)/(N-1)$, if $i \neq j$. The activity coefficients γ_{ij} of the components in every jth phase can be calculated with the UNIFAC routine for these specified compositions of

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the phases. The meaning of this key action is to assign different initial approximations of activity coefficients to the components in various potential phases. This is the way to start from extremely different meanings of concentrations of the components in different phases that have to give the same values of activities to be produced at every iteration (see equation (2)).

A logarithm of the equilibrium constant of reaction of a given component formed from independent components of the system is equail to $-\Delta G$ of the reaction.

$$\ln a_{iJ} = \ln(x_{iJ} \cdot \gamma_{iJ}) = -\Delta G = \sum_{j}^{N} \mu_j v_{iJ} - \mu_{iJ}^{\circ}$$

It means that for every potential phase J the all mole fractions x_{iJ} are calculated as

$$x_{iJ} = \exp\left[-(\mu_i^{\circ} - \sum_{j}^{N} \mu_j v_{ij} + \gamma_{iJ})\right]$$

The exponent is always ≥ 0, thus we can divide all x_i by their sum $X_J = \sum_{i=1}^{N} x_{iJ} : x_{iJ} = \dfrac{x_{iJ}}{X_J}$.

Now the sum of x_i is equal to 1.

The stoichiometric vector of the phase J can be written as $v_{iJ} = v_{iJ} \cdot x_{iJ}$. The value of $-\ln X_J + \sum_{i=1}^{N} \mu_i^{\circ} v_{iJ}$ is assigned to μ_J.

At the next step these phases will be considered as having a fixed composition.

Step 2. Linear programming.

The problem to find the equilibrium assemblage from a set of fixed composition phases can be formulated as:

minimize $G = \sum_{j}^{M} n_j \mu_j$, $n_j \geq 0$ under constraints (3), M=2N is a number of the independent components plus a number of potential phases.

This can be solved with a simplex method. Simplex is a classic finite iteration method of linear programming (Korn and Korn, 1963). The following procedure assumes that at the beginning of step 2 the first N columns in matrix $\|v\|$ define a feasible assemblage of linearly independent phases with μ_i and masses B_i. These conditions are satisfied by the initial assemblage as defined earlier and remain so throughout all iterations. The matrix $\|v\|$ is as follow:

$$
\begin{array}{llll}
1\ 0\ 0...0 & V_{1,N+1}\ V_{1,N+2}\ ...V_{1,2N} & B_1 \\
0\ 1\ 0...0 & V_{2,N+1}\ V_{2,N+2}\ ...V_{2,2N} & B_2 \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
0\ 0\ 0...1 & V_{N,N+1}\ V_{N,N+2}\ ...V_{N,2N} & B_N
\end{array}
$$

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Each column $j = 1,2...$ N represents a "currently stable phase." Each column k=N+1, N+2, ...2N can be interpreted in terms of a reaction relating the phase k to the "currently stable phases". Gibbs energy of the reaction is

$$\Delta G_k = \mu_k - \sum_{j=1}^{N} \mu_j v_{jk}$$

1s.   Each reaction is tested for $G(k) < 0$. If one is found then that phase k is more stable than a linear combination of the "currently stable" phases. At this point the following procedure is started:

2s.   Locate the "currently stable phase" to be replaced by the newly found phase k. The smallest positive B_j/v_{jk} is the criterion. Phase j will be replaced by phase k. Thermodynamic meaning of this is the reaction of new phase formation can go until one of the reactants is used up.

3s.   Replace phase j by phase k.

4s.   Reduce $\|v\|$. This normalizes the reactions to refer to the phases now occupying the basis (the first N positions of the matrix)

Return to step 1s. If none is found terminate the linear programming.

Return to step 1 (nonlinear programming). Repeat in series steps 1 and 2 until for every x_j in every potential phase the condition $\left| 1 - x^{(i+1)}/x^{(i)} \right| \leq \varepsilon$ fulfils, (i) is a number of iteration and ε is a needed accuracy.

As a result of the iterative procedure the basis of the matrix will be occupied by stable phases. Some of this (or all, if the solution is a homogeneous system) will have the same composition. Such phases are considered as parts of one phase, and their amounts B_j should be summarized.

Activity coefficients calculation.

To calculate activity coefficients of compounds in liqiud multicomponent phases as function of composition we used UNIFAC prediction computer program and database. (Fredenslund et al., 1974). The group contribution method is based on the following fundamental assumptions. 1) The logarithm of activity coefficient is a sum of two contributions: a combinatorial part, due to differences in size and shape of the molecules, and the residual part, due to energy interactions. 2) The residual part, the contribution from group interaction, is assumed to be the sum of the individual contributions of each solute group in the solution less the sum of the individual contributions in the pure-component environment. 3) The individual group contributions in any environment containing groups of kinds *1, 2 ... N* are asuumed to be only a function of group concentrations and temperature (Van Ness et al., 1973,

Reid et al., 1987). The database on group interaction parameters had been developed as a result of processing of large amount of experimental data.

The program is written in FORTRAN-IV and consists of the following modules.

1. Main program EQSIMFR minimizes Gibbs energy of the system and outputs the result of calculations. It calls UNIFAC subroutine first time to read input data and to calculate parameters for specified system and N (number of components) times at every iteration to calculate activity coefficients of the components in potential phases at their current concentrations. The program also calls SIMPLEX subroutine to search the assemblage of fixed composition phases at every iteration.

We used UNIFAC program and database of Fredenslund et al. (1992) without significant changes. The only corrections were to convert the program to a subroutine and to separate the part of the routine, which searches in the database and calculates parameters for specified system to execute it one time.

We kept input without any changes. The information about the phase composition in Fredenslund et al. program is used in the model as a bulk composition of the system

<u>An example of the input(file "input.txt").</u>

(1) PROP. GLYCOL	4	*Name of the component(20 positions) and*	
(2) ETHANOL	3	*a number N of different secondary groups in the molecule*	
(3) WATER	1		
(4) BENZENE	1		

```
1   1   3   2   1   3   2   14   Number of times secondary group I appears in molecule J.
1   1   2   2   1   14            Identification number of group I in molecule J, secondary
1   17                           group number
6   9
302.50                          temperature
0.005    0.06      0.935   0.1  numbers of moles (or mole fractions) of the components
                                 in mixture
```

<u>An example of the output (file "result")</u>

TEMPERATURE   302.50 K

           PHASE 1

           0.1694 MOLES

n COMPONENT   MOLE   MOL.FRACTION ACTIVITY   ACT.COEFF.

1 (1) PROP. GLYCOL 0.50006D-02 0.29514D-01 0.33594D-01 1.138

2 (2) ETHANOL   0.59736D-01 0.35257D+00 0.38978D+00 1.106

3 (3) WATER   0.47311D-02 0.27923D-01 0.99966D+00 35.800

4 (4) BENZENE   0.99964D-01 0.59000D+00 0.59293D+00 1.005

PHASE 2

0.9306 MOLES

n COMPONENT	MOLE	MOL.FRACTION	ACTIVITY	ACT.COEFF.
1 (1) PROP. GLYCOL	0.31332D-06	0.33670D-06	0.33594D-01	99773.219
2 (2) ETHANOL	0.26361D-03	0.28328D-03	0.38978D+00	1375.930
3 (3) WATER	0.93027D+00	0.99968D+00	0.99968D+00	1.000
4 (4) BENZENE	0.36295D-04	0.39003D-04	0.59293D+00	15202.278

BALANCE (MOLES)

COMPONENT	PHASE 1	PHASE 2	BULK CALC.	BULK INPUT
(1) PROP. GLYCOL	0.0049997	0.0000003	0.0050000	0.0050000
(2) ETHANOL	0.0597364	0.0002636	0.0600000	0.0600000
(3) WATER	0.0047313	0.9302687	0.9350000	0.9350000
(4) BENZENE	0.0999637	0.0000363	0.1000000	0.1000000

Concluding remarks.

It was noted that the model could also take into account chemical interactions between substances. For this goal it takes 1) input standard chemical potentials μ^o of the substances at specified temperature and 2) the matrix $\|\nu\|$ contains real stoichiometric (in chemical element or in group terms) compositions of the substances.

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AD NUMBER	DATE	DTIC ACCESSION NOTICE

20010502 049

1. REPORT IDENTIFYING INFORMATION

A. ORIGINATING AGENCY
Vernadsky Institute of geochemistry & analytical chemistry, Russia.

B. REPORT TITLE AND/OR NUMBER
Development of a new program to calculate liquid-liquid phase equilibria in multicomponent system (Gibbs of energy substance)

C. MONITOR REPORT NUMBER
R&D8965-EN-01

D. PREPARED UNDER CONTRACT NUMBER
N68171-00-M-6199

2. DISTRIBUTION STATEMENT
APPROVED FOR PUBLIC RELEASE

DISTRIBUTION UNLIMITED

FINAL

DTIC OCT 95